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Standard Method of Test for

AROMATICS IN LIGHT NAPHTHAS AND AVIATION GASOLINES BY GAS CHROMATOGRAPHY[1]

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ASTM Designation: D 2267 – 68

This Standard of the American Society for Testing and Materials is issued under the fixed designation D 2267; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

1. Scope

1.1 This method covers the determination of benzene, toluene, C_8, and heavier aromatics, and total aromatics in the concentration range from 1.0 to 30 percent of the individual aromatic compounds listed above in the following products: (*1*) aviation gasolines described in ASTM Specifications D 910, for Aviation Gasolines;[2] (*2*) reformer products having a final boiling point below 350 F (177 C); and (*3*) reformer feed and other petroleum products having a final boiling point below 300 F (149 C). The results are reported to the nearest 0.1 percent by liquid volume.

NOTE 1—ASTM Method D 2600, Test for Aromatic Traces in Light Saturated Hydrocarbons by Gas Chromatography,[3] should be used to determine aromatics in concentrations below 1.0.

2. Summary of Method

2.1 The sample is introduced into a gas chromatographic column containing a strongly polar liquid phase. The polar phase has very little affinity for saturated and olefinic hydrocarbons, while exhibiting a pronounced selectivity for aromatics. This selectivity results in the elution of all saturated and olefinic hydrocarbons in the products described above prior to the elution of benzene. Either a thermal conductivity or flame ionization detector may be used. Calibration is performed by using synthetic blends of the aromatic compounds charged at the same constant volume as is used to analyze the sample. *N*-undecane or *n*-dodecane is used as an internal standard. Typical retention times are shown in Table 1 and a typical chromatogram is shown in Fig. 1.

NOTE 2—Reference should be made to ASTM Recommended Practice E 260, General Gas Chromatography Procedures.[4]

NOTE 3: **Caution**—Light aromatic hydrocarbons are toxic. Special precautions should be taken when handling such materials to avoid inhaling the vapor. If some of the liquid is accidentally spilled on the skin, the affected part should be washed immediately with soap and water.

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[1] Under the standardization procedure of the Society, this method is under the jurisdiction of the ASTM Committee D-2 on Petroleum Products and Lubricants. A list of members may be found in the ASTM Year Book.
Current edition accepted Sept. 13, 1968. Originally issued 1964. Replaces D 2267 – 67.

[2] Appears in this publication.

[3] *Annual Book of ASTM Standards*, Part 18.

[4] *Annual Book of ASTM Standards*, Part 30.

3. Apparatus

3.1 *Chromatograph*—Any chromatographic instrument may be used which has the following performance and characteristics:

3.1.1 *Sensitivity*—An over-all sensitivity sufficient to detect 0.1 volume percent of any aromatic compound of interest with a peak height of at least 2 mm without loss of resolution as defined in 3.1.3.

3.1.2 *Sample Inlet System*—A sample inlet system that allows a constant volume of liquid sample to be injected.

3.1.3 *Column*—Inject Blend 1, Table 2, into the chromatograph and record the chromatogram. Any column and conditions may be used provided, under conditions of the test, *n*-decane is eluted prior to benzene and the depth of the valley after *n*-decane is not less than 50 percent of the height of the decane peak. The benzene, toluene, and C_8 and heavier aromatics must be completely resolved from each other, and the internal standard, *n*-undecane or *n*-dodecane, must be completely separated from all aromatic compounds.

Note 4—Column, materials, and conditions that have been found suitable for this method are listed in Table 3. Typical instructions for preparing such columns may be found in Recommended Practice E 260.

3.2 *Strip Chart Recorder*—A recording potentiometer with a full-scale deflection of 10 mV or less should be used. The full-scale response of the recorder should not exceed 2 s. If a manual method of integration (such as triangulation, paper cut-out or planimeter) is employed, the chart speed should be at least 60 in./h (150 cm/h) in order to minimize errors in peak area measurement. This requirement is waived if a ball-and-disc or an electronic integrator is employed.

3.3 *Micro Syringe*, 10-μl capacity, for sample introduction.

3.4 *Volumetric Flasks*.

3.5 *Volumetric Pipets*.

3.6 *Tubing*, copper, aluminum, or stainless steel.

3.7 *Analytical Balance*.

4. Reagents and Materials

4.1 *Liquid Phase for Column*—See Note 4.

4.2 *Solid Support*—See Note 4. If an open tubular column is used, a solid support is not necessary.

4.3 *Solvent for Liquid Phase*—Methylene chloride has been found satisfactory.

4.4 *Carrier Gas*—See Note 4.

4.5 *N-hexane, n-Heptane or Isooctane*, 99 mole percent minimum containing less than 0.05 of aromatic material.

TABLE 1—TYPICAL RETENTION TIME, MINUTES

Column	1	2	3	4	5
n-decane	2.3	6.8	2.6	2.0	10.2
Benzene	2.9	7.6	3.0	3.3	15
Toluene	4.5	11.4	4.3	5.3	19.1
Ethylbenzene	6.6	17.2	6.0	7.7	23.3
n-undecane	...	10.1	3.8	...	...
n-dodecane	5.85	...	...	4.7	17.3

4.6 *Benzene, Toluene, and Ethylbenzene*, 99.5 mole percent minimum.

4.7 *n-Decane and Either n-Undecane or n-Dodecane*—Either the C_{11} or C_{12} normal paraffin may be used as an internal standard according to the requirements in 3.1.3.

5. Sample Handling

5.1 Due to the volatility of these materials and the tendency toward change in composition, store all samples and standard blends at a temperature of 45 to 60 F (7 to 15 C). Do not open the sample or standard container at liquid temperatures above 60 F (15 C). Transfers from the container to the chromatograph should be made only when the liquid in the container is within the temperature range indicated.

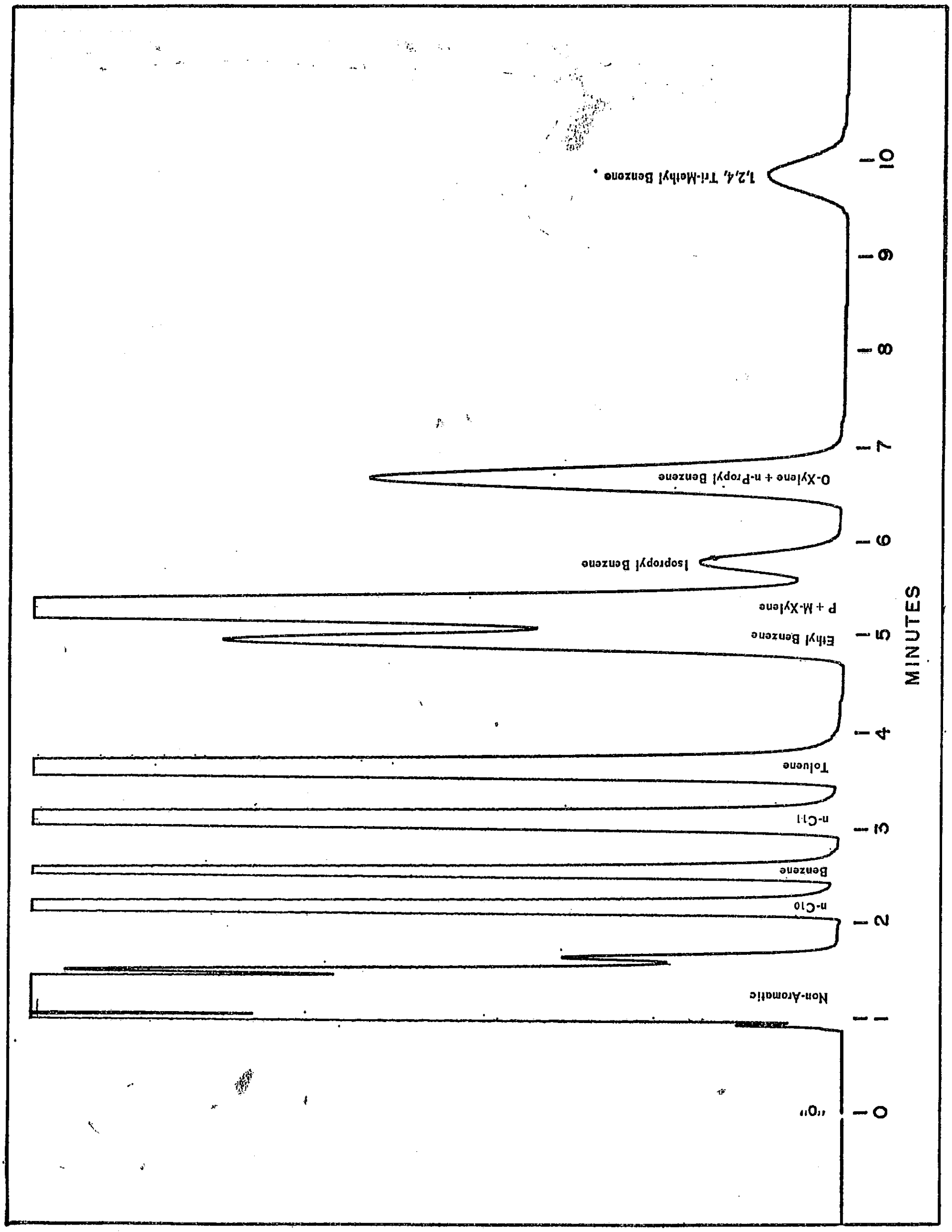

FIG. 1—Typical Chromatogram Using Table 3, Column 3.

6. Calibration

6.1 *Preparation of Standards*—Prepare three standard blends indicated as Blend 1, 2, and 3 in Table 2. To do this, pipet the exact volume of each hydrocarbon indicated into a 100-ml flask. Fill to the 100-ml mark with one of the solvents listed in 4.5 and mix by inverting several times.

TABLE 2—COMPOSITION OF STANDARD BLENDS

Blend No.	nC_{10}	Internal Standard	Benzene	Toluene	Ethyl Benzene
1........	5	10.0	15.0	15.0	15.0
2........	...	10.0	5.0	5.0	25.0
3........	...	10.0	25.0	25.0	5.0
4........	1	...	0.5	0.5	0.5

6.2 Select the instrument conditions and sample size so as to give the necessary sensitivity and resolution. Inject each standard blend into the chromatograph at least twice, using the same volume of sample and instrument conditions. If a sensitivity of less than maximum is needed to measure the *n*-decane, internal standard and aromatic peaks,

TABLE 3—TYPICAL COLUMNS AND CONDITIONS

	1	2	3	4	5
Column:					
Liquid phase, material ..	DEGS	PEG-400	TCEPE	TCEPE	TCEP
Weight percent.........	20	...	10	15	20
Solid support, material...	Chrom. P	...	Chrom. P	Chrom. P	Chrom. P
Mesh size..............	60 to 80	...	60 to 80	60 to 80(S)	60 to 80
Treatment.............	None	...	AW	AW	AW
Length, ft.............	8	100	15	16	20
Inside diameter, in......	0.22	0.01	0.063	0.063	0.180
Temperature:					
Sample inlet system, deg C............	266	150	250	300	190
Detector, deg C........	102	86	175	260	215
Column:					
Isothermal, deg C.....	102	86	100	100	...
Programmed, deg C/min..............	...	...	...	...	4
Initial temperature, deg C............	...	...	...	...	50
Constant finally, min..	...	...	...	...	5
Final temperature, deg C............	...	...	...	...	150
Carrier gas, material......	helium	nitrogen	nitrogen	helium	helium
Flow rate, cm³/min.....	100	2.5	2.0	40	75
Detector, type............	T.C.	F.I.	F.I.	F.I.	T.C.
Voltage (or mA)........	12 V	...	...	...	200 mA
Recorder range, mV.......	1	10	5	1	1
Sample size, µl	5	2	5	1.5	1.5
Split, ratio.............	...	250:1	100:1	...	...
Speed, in./h..............	30	30	30	30	30

Abbreviations:
DEGS—Diethylene glycol succinate
PEG—Polyethylene glycol
TCEPE—Tetracyano ethylated pentaerythritol
TCEP—1,2,3 Tris (2 cyano ethoxy) propane
Chrom. P—Chromosorb P
AW—Acid Washed
T.C.—Thermal conductivity
F.I.—Flame ionization
(S)—Sieved

change the attenuation so that the peaks are measured at not less than 25 percent of full scale.

6.3 On Blend 1 measure the height of the *n*-decane peak and the height of the valley between it and benzene. Express both on a common attenuation basis. Divide the height of the valley above the base line by the total height of the *n*-decane peak. This value must not exceed 0.5 for the column and conditions to be used.

6.4 Measure the area of all aromatic and internal standard peaks by any of the following means: triangulation, planimeter, paper cut-out, ball-and-disc integrator, or electronic integrator.

TABLE 4—RELATIVE RESPONSE FACTORS[a]

Concentration Range	Aromatics in Standard, ml	Benzene	Toluene	C_8 +
1 to 10......	5	R_{62}	R_{72}	R_{83}
10 to 20......	15	R_{61}	R_{71}	R_{81}
20 to 30......	25	R_{63}	R_{73}	R_{82}

[a] The first digit of the subscript refers to the carbon number of the aromatic compound and the second digit refers to the blend number.

NOTE 5—Because the C_8 and heavier compounds may not be completely resolved, peak height times one half the width or retention time must not be used as a means of measuring the area.

6.5 If a different attenuation was used for part of the chromatogram, correct to a constant attenuation basis by multiplying the areas where a lower sensitivity was used by the ratio:

$$\frac{S_I}{S_a}$$

where:

S_I = the attenuation sensitivity used for the internal standard peak, and

S_a = attenuation sensitivity used for the aromatic peak.

6.6 *Relative Response Factors*—Calculate relative response factors for each aromatic compound at each concentration level relative to that of the internal standard as follows:

$$R_{ij} = \frac{A_s/10}{A_a/v}$$

where:

R_{ij} = relative response factor for each aromatic compound at each concentration level,

A_s = area of the internal standard peak in arbitrary units corrected for attenuation,

10 = volume of internal standard in the standard blend,

A_a = area of the aromatic peak in arbitrary units corrected for the difference in attenuation, and

v = volume of aromatic in the standard blend.

6.7 Using the average calculated response factors, tabulate the factors for each aromatic compound by concentration range as shown in Table 4.

7. Procedure

7.1 Follow the instructions in 5. Sample Handling. Pipet exactly 1.0 ml of internal standard into a 10-ml volumetric flask. Fill to the 10-ml mark with sample and mix by inverting several times.

7.2 Using the exact instrument conditions as were used in the calibration, inject the same volume of sample containing the internal standard. Change the attenuation if necessary so as to measure the area of the internal standard and aromatic peaks with not less than 25 percent chart deflection on attenuated peaks.

8. Calculations

8.1 Measure the area of the internal standard and aromatic peaks in the same manner as was used for calibration. If a different attenuation was used for part of the chromatogram, correct to a constant attenuation basis by multiplying the area of the aromatic peaks by the ratio:

$$\frac{S_I}{S_a}$$

where:

S_I = attenuation sensitivity used for the internal standard peaks, and

S_a = attenuation sensitivity used for the aromatic peak.

8.2 Calculate the concentration of benzene, toluene, C_8, and heavier aromatics as follows:

$$V = \frac{A_a \times R_{ij} \times 10}{A_s \times 0.9}$$

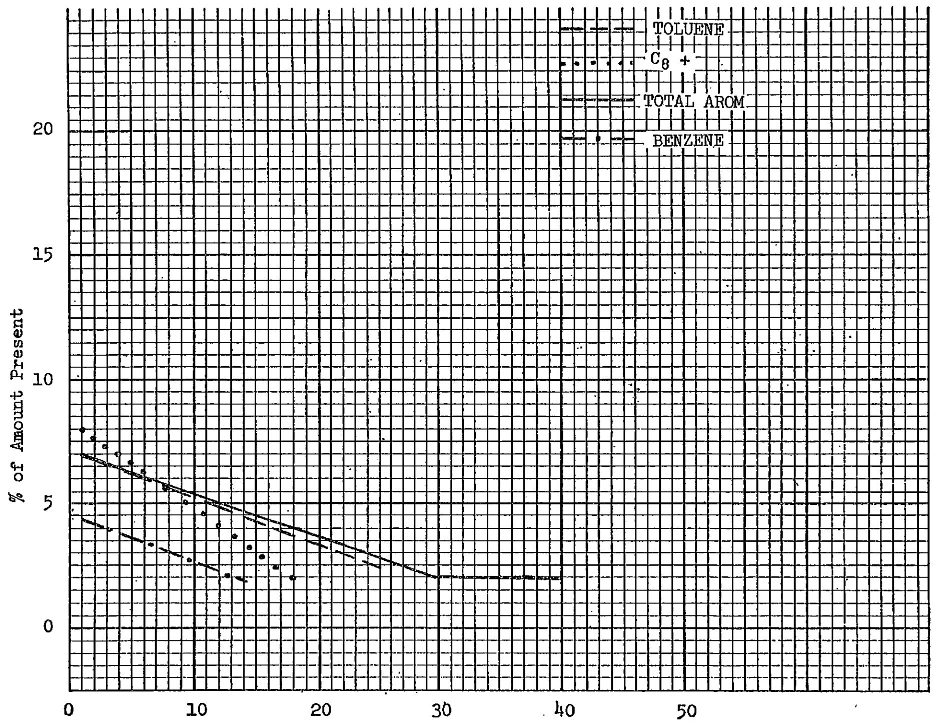

FIG. 2—Repeatability.

where:

V = volume percentage of the aromatic compound(s),

A_a = area of the aromatic peak corrected to a constant attenuation,

R_{ij} = relative response factor for the aromatic compound according to concentration of the aromatic compound in the sample (Note 6),

10 = volume percent of internal standard,

A_s = area of the internal standard peak, and

0.9 = factor to correct for the dilution by the internal standard.

Use the relative response factor for ethylbenzene for all C_8 and heavier compounds.

NOTE 6—It may be necessary to calculate approximate answers in order to determine which response factor to use according to the concentration of the aromatic compound in the sample.

8.3 *Total Aromatics*—Add the amounts of each aromatic compound found to obtain the volume percent of total aromatics in the sample.

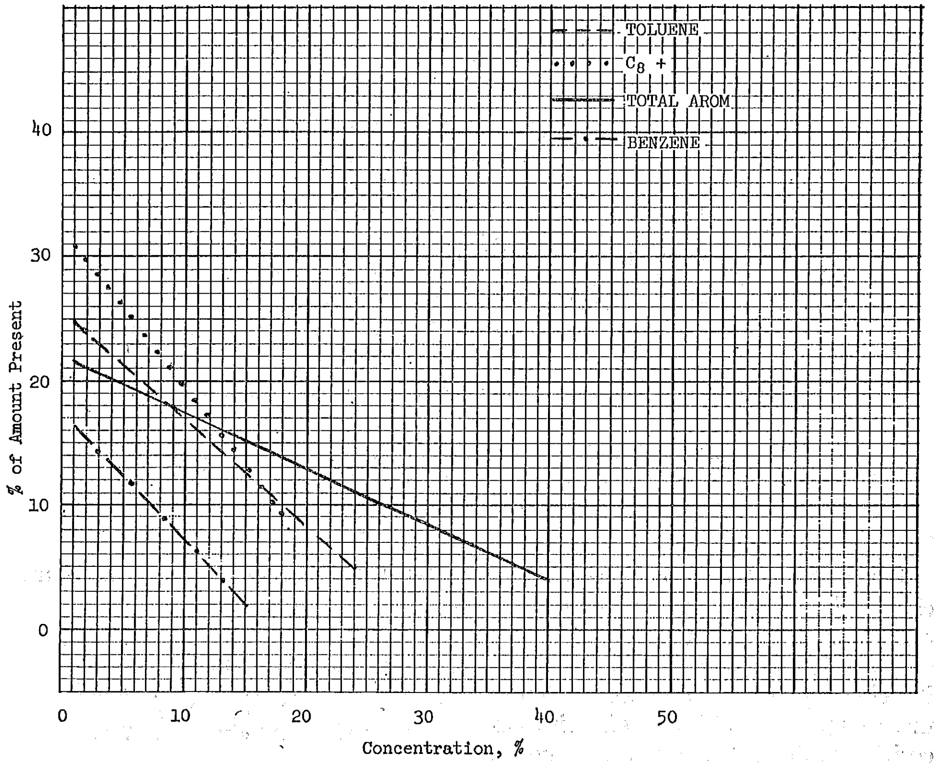

FIG. 3—Reproducibility.

8.4 *Report*—Report the volume percentage to the nearest 0.1 percent by volume.

9. Precision

9.1 The criteria shown in Figs. 2 and 3 should be used for judging the acceptability of results (95 percent probability). The precision statements are based on results from five laboratories analyzing five samples and should be considered tentative, pending further work and statistical evaluation. Electronic integrators were used by all of the cooperating laboratories. Less precise results may be obtained if other methods of measurement are used.

9.1.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if they differ by more than the amounts shown in Fig. 2 for repeatability as percent of the average amount present.

9.1.2 *Reproducibility*—The results submitted from two laboratories should be considered suspect if they differ by more than the amount shown in Fig. 3 for reproducibility as percent of the average amount present.